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PRELIMINARY OBSERVATIONS ON A REVERSIBLE STRUCTURAL CHANGE IN COBALT FLUOSILICATE HEXAHYDRATE

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It has been recently observed in our laboratory (Majumder and Datta, communicated for publication) that rhombohedral crystals of cobalt fluosilicate hexahydrate, suspended along the trigonal axis, start showing magnetic anisotropy when cooled below 248°K. Further, this change in magnetic behaviour has been found to be reversible with temperature. This phenomenon evidently indicates some reversible structural change in the crystals at the said low temperature, hence X-ray investigation was taken up to find out the nature of the change.

From the magnetic observations it appears that whatever the change it undergoes, a single crystal remains a single crystal in the new phase. So, oscillation and Weissenberg photographs could be obtained with crystals cooled well below the reported transition point. For the preliminary observations reported here, all the photographs were taken with crystals oscillating about the trigonal axis, in a Weissenberg camera equipped with a gas-flow type cooling system.

The Weissenberg photograph thus obtained at low temperature shows that corresponding to each spot appearing in the similar photograph taken at room temperature, there is a pair of spots, one of which lies at a slightly different Bragg angle than the other. The photograph thus contains two distinct families of spots, indicating that the diffraction pattern obtained at a temperature below the magnetic transition point corresponds to two different coexisting phases.

Both the families of spots can be indexed by triply primitive hexagonal cells (as is the case for a rhombohedral structure referred to hexagonal axes), with parameters $a = 9.68 \pm .01$ Å and $9.51 \pm .01$ Å respectively for the two. It may be mentioned here that the value of the corresponding parameter for cobalt fluosilicate hexahydrate at room temperature is 9.31 Å (Hassel and Salvesen, 1927).

Information regarding the cell dimensions along the *c*-axis are obtained from the oscillation photograph taken below transition temperature. Here also the splitting up of the spots into pairs is observed, but since the members of the

same pair are found to lie on the same layer line, it is evident that the c-axes of both the phase are indentical in direction and repeat distance. Since the cooling attachment used permits recording of only half the diffraction pattern (lying on one side of the equatorial layer line), the repeat distance along the common c-axis of the two phases can only be determined very roughly, and is found to be 9.8Å. Corresponding value for the crystal at room temperature is 9.695Å (Hassel and Salvesen, loc. cit.).

The most interesting feature regarding the two low temperature phases is revealed on close observation of the intensities of the spots in the Weissenberg photograph. While the intensities of the spots corresponding to the phase with $a = 9.68 \pm .01$Å, reveal a three-fold symmetry, no evidence of such a symmetry is observed in the intensities of those corresponding to the second phase. Hence the second phase is only pseudo-hexagonal, with $a = b = 9.51 \pm .01$Å and $\gamma = 120°$. This lack of three-fold symmetry explains the appearance of magnetic anisotropy below the transition temperature.

Another interesting feature of the transition is that even when a crystal was pre-cooled for one hour before starting the X-ray exposure (which extended for two hours in this particular case), the diffraction pattern showed the simultaneous existence of both the phases. However, it was not possible to decide at present whether the difference in cooling treatment made any difference in the relative concentration of the two phases.

Reversibility of the transition has also been tested by taking the photograph of a crystal brought back to room temperature after the low temperature exposure, when the same diffraction pattern as that recorded initially at room temperature is obtained.

Further detailed work on the structures of the phases and their relationship with the original structure of the crystal is in progress.

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